

AD-A285 044



Dist. A

Form Approved  
OMB No. 0704-0188

## MENTATION PAGE

Estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson D, Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	8/16/94	Report: July 1992-July 1994	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
Aryl Gels and Related Materials. Synthesis and Characterization of a New Class of Microporous Materials		61102F 2303 CS	
6. AUTHOR(S)		7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(S)	
Kenneth J. Shea		Univ of California, Irvine Room 115, Administration Bldg. Irvine, CA 92717	
8. PERFORMING ORGANIZATION REPORT NUMBER		9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(S)	
AFOSR-TR-94 0557		AFOSR/NCNL Building 410, Bolling AFB DC 20332-6448 Dr. Lee	
10. SPONSORING / MONITORING AGENCY REPORT NUMBER			
F49620-92-J-0379			
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.		A	
13. ABSTRACT (Maximum 200 words)			
<p>The objective of this program is the synthesis and characterization of new families of optically responsive materials for use in optical device fabrication. The materials that have been developed are <i>polysilsesquioxanes</i>, hybrids of organic network polymers and inorganic oxides.</p> <p>The materials are prepared by sol-gel techniques employing <i>molecular building blocks</i> that contain a variable organic component and an inorganic oxide precursor. The resulting materials are <i>molecular composites</i> with no phase boundary between the organic and inorganic domains.</p> <p>Where the organic component of the molecular building block contains a chromophore with known NLO properties, optically responsive materials can be produced. In our efforts we have produced optical quality thin films by a combined sol-gel/electric field poling technique. The resulting poled thin films exhibit <math>d_{33}</math> and <math>r_{33}</math> figures of merit of 35-37 (pm/V) and 9-10 (pm/V). These values are comparable to that of lithium niobate. Work is continuing to enhance the <math>d_{33}</math> and <math>r_{33}</math> values as well as to improve the optical stability at elevated temperatures.</p> <p>In a relatively new effort we are developing methods for preparing optically transparent films and monoliths doped with quantum sized transition metal clusters. We have made an initial discovery that these materials have extremely high <math>\chi^3</math> coefficients. Work is continuing in this area to understand the origins of this effect.</p>			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
Hybrid materials, molecular composites, sol-gel chemistry, NLO materials		16	
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE	
UNCLASSIFIED		UNCLASSIFIED	
19. SECURITY CLASSIFICATION OF ABSTRACT		20. LIMITATION OF ABSTRACT	
UNCLASSIFIED			

**Air Force Office of Scientific Research  
Research Grant F49620-92-J-0379  
Overview of Research Accomplishments  
July 1992 - July 1994**

**Abstract**

The objective of this program is the synthesis and characterization of new families of optically responsive materials for use in optical device fabrication. The materials that have been developed are *polysilsesquioxanes*, hybrids of organic network polymers and inorganic oxides.

The materials are prepared by sol-gel techniques employing *molecular building blocks* that contain a variable organic component and an inorganic oxide precursor. The resulting materials are *molecular composites* with no phase boundary between the organic and inorganic domains.

Where the organic component of the molecular building block contains a chromophore with known NLO properties, optically responsive materials can be produced. In our efforts we have produced optical quality thin films by a combined sol-gel/electric field poling technique. The resulting poled thin films exhibit  $d_{33}$  and  $r_{33}$  figures of merit of 35-37 (pm/V) and 9-10 (pm/V). These values are comparable to that of lithium niobate. Work is continuing to enhance the  $d_{33}$  and  $r_{33}$  values as well as to improve the optical stability at elevated temperatures.

In a relatively new effort we are developing methods for preparing optically transparent films and monoliths doped with quantum sized transition metal clusters. We have made an initial discovery that these materials have extremely high  $\chi^3$  coefficients. Work is continuing in this area to understand the origins of this effect.

1994-30993

**94-30993**



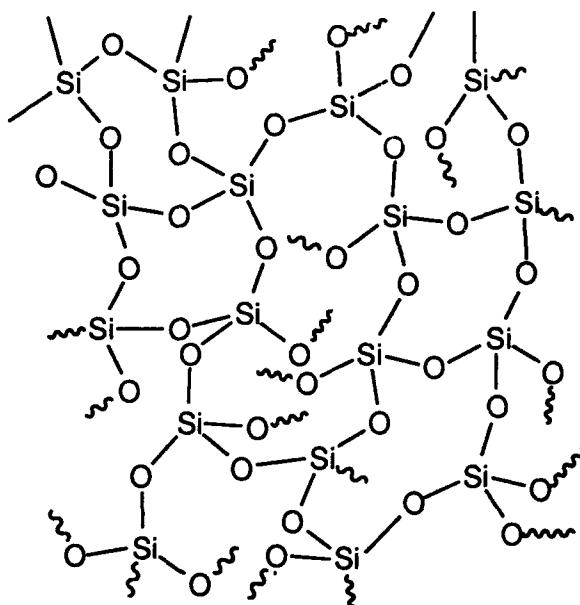
AFS

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65

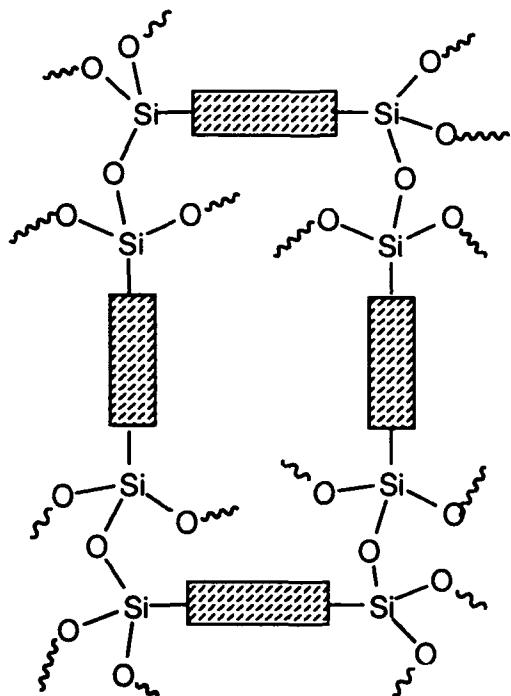
Air Force Office of Scientific Research  
Research Grant F49620-92-J-0379  
Overview of Research Accomplishments  
July 1992 - July 1994

*Introduction*

The principal objective of this research program is the synthesis and characterization of new families of optically responsive materials for use in optical device fabrication. The materials that we have developed for this application are polysilsesquioxanes, hybrids of organic network polymers and inorganic oxides.



Silica

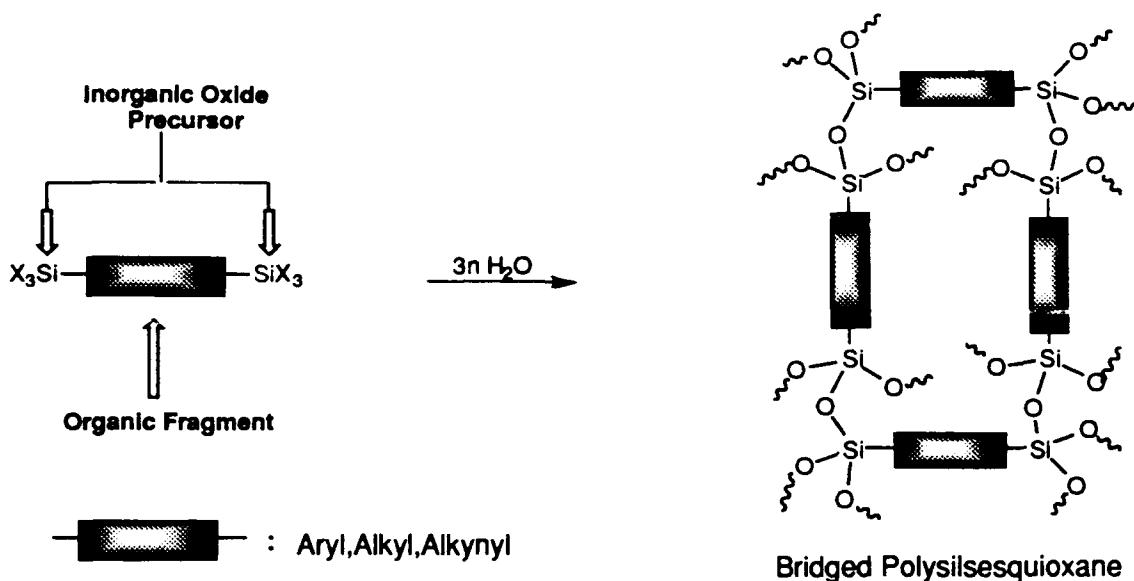


Bridged Polysilsesquioxane

Polysilsesquioxanes are *molecular composites*, hybrid materials that do not have a phase boundary between the organic and inorganic domains. Polysilsesquioxanes are synthesized by sol-gel chemistry from molecular building blocks that contain a variable organic component and an inorganic oxide precursor (see the following figure).

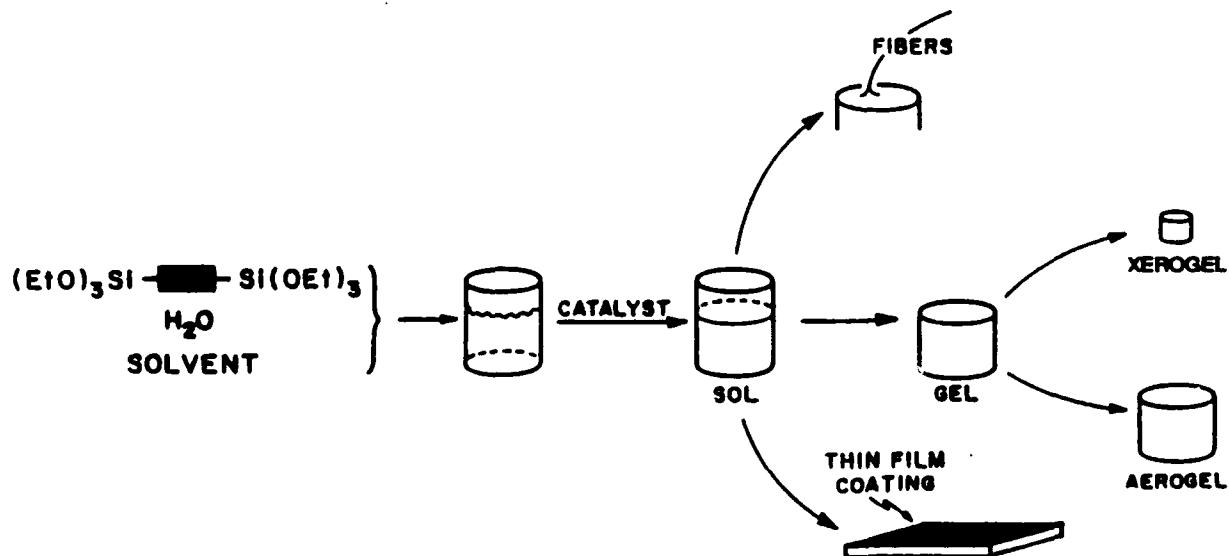
Avail. Codes	Avail. Codes
Dist	Spec'd
A-1	

## MOLECULAR COMPOSITE

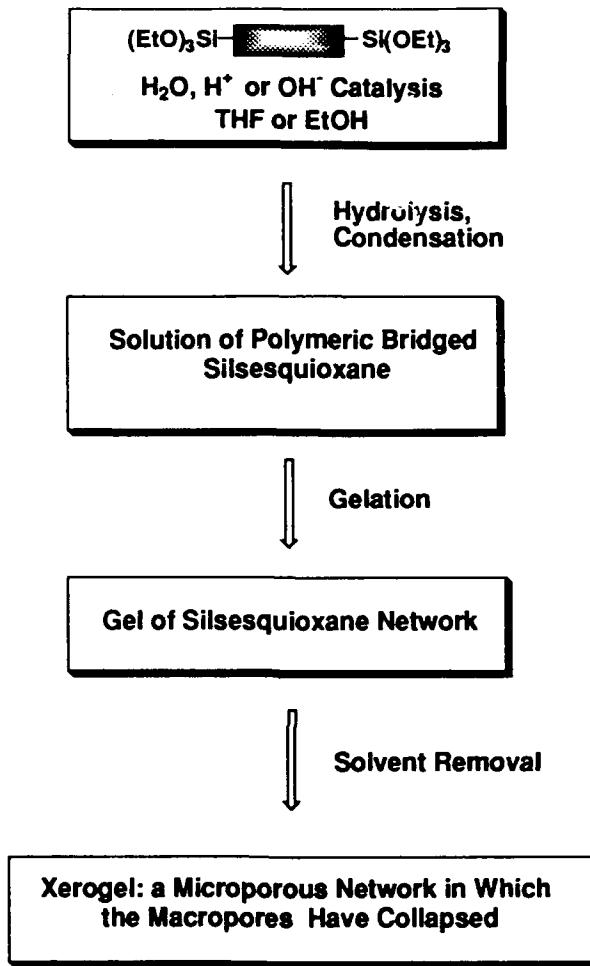


Solutions of monomer, solvent, water and catalyst can be spin-cast into thin films, drawn to produce fibers, or, following gelation, processed into optically transparent monoliths (xerogels) or aerogels by supercritical solvent extraction (see the following figure).

## BRIDGED POLYSILSESQUIOXANES



## SOL-GEL PROCESSING



Realization of the overall objectives of the research program requires a combination of synthetic organic chemistry, materials synthesis and characterization and quantitative evaluation of the optical behavior of the resulting NLO materials. This effort requires collaboration with groups that have expertise in the evaluation of NLO materials.

### *Design Criteria*

There are a number of criteria that must be met before the polysilsesquioxanes are successfully adapted to NLO device fabrication. Many of these issues are interrelated. We believe that polysilsesquioxanes can provide the best solution for these requirements. Some of these criteria are listed below:

**A. Chromophore Variability.** The synthesis of NLO responsive materials should be very general to allow incorporation of a variety of chromophores. The synthetic methodology that we have developed permits us to convert most interesting organic chromophores into sol-gel processable monomers (optiphores).

**B. Optiphore Loading.** Optimum NLO response requires that the amount or loading of chromophore in the material be high. Since every monomer contains the chromophore, polysilsesquioxanes easily satisfy this requirement.

**C. Processability.** Sol solutions must be processable into optical quality thin films and, for device fabrication, a variety of geometric shapes. The sol-gel process is ideally suited for this task.

**D. Optical Quality.** Films and devices must be optically transparent. An optical quality film or device fabricated from hybrid materials requires control over porosity of the material and phase separation of the inorganic and organic components. The *molecular composite* approach eliminates phase separation problems and we have considerable experience in the control of porosity in these materials.

**E. Compatibility with Poling.** Conditions used for sol-gel processing must contain low amounts of ionic substances to minimize dielectric breakdown (arcing) during poling.

**F. High Tg.** For  $\chi^2$  performance the bulk material must posses oriented chromophores. In order for the NLO response to be stable over a wide temperature range, segmented motion of polymer chains in the condensed material must be minimized. Highly condensed polysilsesquioxanes do *not* exhibit a Tg and are capable therefore of producing a persistent NLO response at elevated temperatures over prolonged periods of time. Furthermore, many xerogels are stable to temperatures up to 500 °C.

#### *Summary of Results*

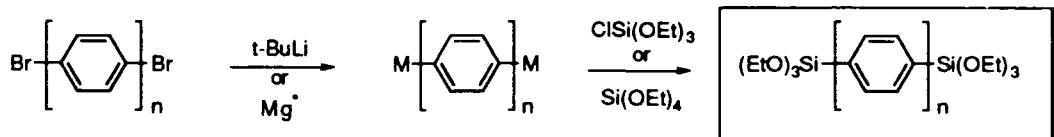
A summary of the developments over the last two years with particular attention to the points raised above is given below:

## Monomer Synthesis

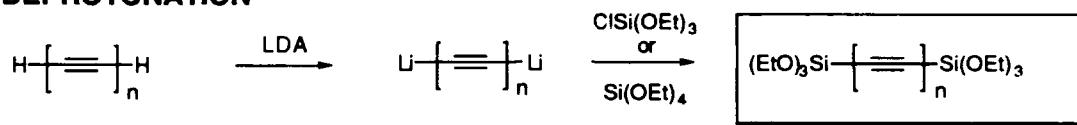
The molecular building block approach benefits from a wide variety of synthetic transformations for attaching triethoxysilyl groups ( $-\text{Si(OEt)}_3$ ) to organic molecules. The following figure outlines some of the synthetic transformation that we have utilized to accomplish this task. These transformations provide us with great flexibility in the synthesis of molecular building blocks that can be used for assembly of polysilsesquioxanes.

### MONOMER SYNTHESIS

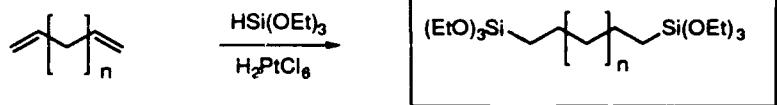
#### METALLATION



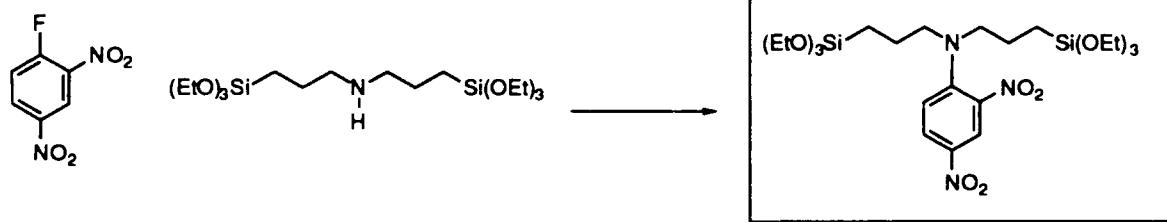
#### DEPROTONATION



#### HYDROSILATION

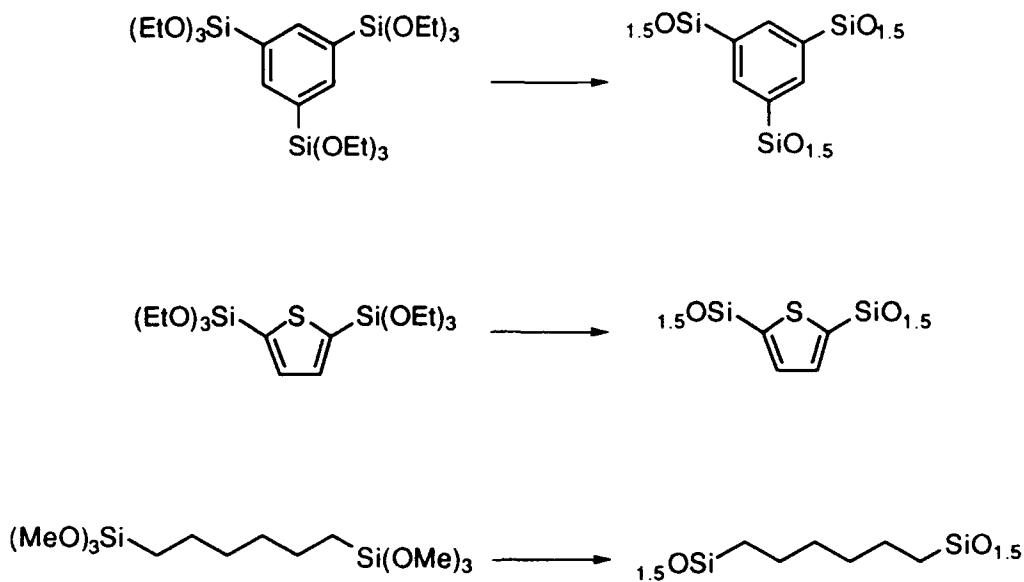


#### NUCLEOPHILIC SUBSTITUTION



### Synthesis and Characterization of Polysilsesquioxanes

Since our initial reports of the synthesis and characterization of aryl bridged polysilsesquioxanes<sup>1,2</sup> we have extended the range of molecular building blocks used for the synthesis of these materials. Representative examples are shown in the following figure.<sup>3</sup>



The resulting dried xerogels are brittle glassy substances that have internal surface areas ranging from 400 to 700 m<sup>2</sup>/g. The average pore size falls in the low mesopore to micropore domain (<35 Å).

### Molecular Determinants of Porosity

The technological applications of polysilsesquioxanes require an understanding of the relationship of the morphology of the material to the molecular building block. For example, in a number of applications, porosity is an important property of the bulk material. What is the relationship between the shape and structure of the organic fragment and porosity (internal surface area and pore size distribution)? For a number of applications, a fully condensed, *non-porous* polysilsesquioxane would be desirable. What are the molecular building block requirements for this? Since porosity arises from the choice of molecular building block *and* processing conditions, we must understand how these factors influence the final result.

To understand how the molecular building block affects porosity, we examined the surface area and pore size of xerogels prepared from a series of alkylene-bridged bistriethoxysilyl alkanes (see following table).<sup>4</sup> The xerogels were prepared by a uniform set of sol-gel and processing conditions.

## REQUIREMENTS FOR POROSITY

	Degree of Functionality			
	Spacer Properties			
	Sol-Gel Reaction Conditions			
	Gel Processing Conditions			
	EtOH GELS (OH <sup>-</sup> )	THF GELS (H <sup>+</sup> )		
	SA(m <sup>2</sup> /g)	pore dia. (nm)	SA(m <sup>2</sup> /g)	pore dia. (nm)
<chem>(EtO)3Si-CH2-CH2-Si(OEt)3</chem>	729	4.3	641	2.3
<chem>(EtO)3Si-CH2-CH2-CH2-Si(OEt)3</chem>	710	4.1	---	---
<chem>(EtO)3Si-CH2-CH2-CH2-CH2-Si(OEt)3</chem>	564	4.3	6.6	---
<chem>(EtO)3Si-CH2-CH2-CH2-CH2-CH2-Si(OEt)3</chem>	448	6.7	3.2	---
<chem>(EtO)3Si-CH2-CH2-CH2-CH2-CH2-CH2-Si(OEt)3</chem>	94	19.7	5.6	---
<chem>(EtO)3Si-CH2-CH2-CH2-CH2-CH2-CH2-CH2-Si(OEt)3</chem>	5	---	---	---

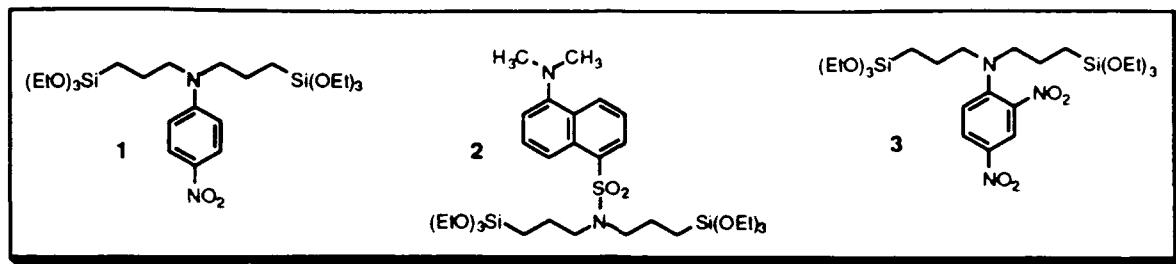
We have found that as the *flexibility* and *length of the alkylene spacer* increased, the net surface area decreased. Beyond a 12 carbon atom chain, fully condensed non-porous materials are produced. This result suggests that some degree of rigidity in the molecular building block is necessary to sustain porosity. Monomers that contain large, flexible organic groups result in fully collapsed, non-porous networks. One also notes from the data that the choice of catalyst influences the porosity of the resulting xerogel. DSC and TGA analysis of alkylene bridged polysilsesquioxanes are distinguished by the absence of a Tg. In addition, the onset of decomposition occurs at temperatures approaching 500 °C.

These results provided us with some understanding of how the choice of molecular building block and processing conditions influence the morphology of the resulting material. In general, the thermal characteristics of these highly condensed materials are similar to that of thermosets.

### Synthesis of NLO Molecular Building Blocks and Their Sol-Gel Processing into NLO Thin Films.

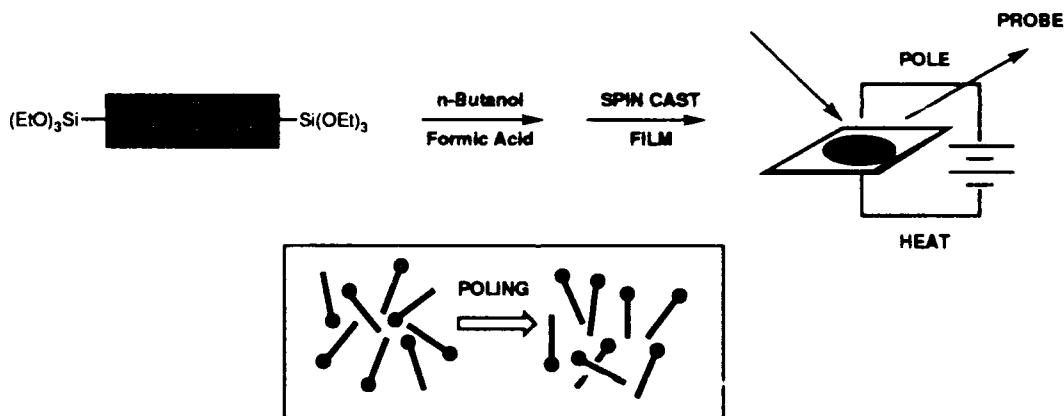
The preceding findings guided our choice for formation of NLO thin films using a sol-gel processable molecular building block. Three monomers (**1-3**) were synthesized by techniques outlined previously.

## SOL-GEL PROCESSABLE NLO CHROMOPHORES



A number of solvent and catalyst systems were explored to permit spin casting of optically transparent thin films. The optimum conditions are shown in the figure below. Of particular note is the choice of n-butanol as the solvent which controls the rate of evaporation during spin casting and the use of formic acid as the catalyst which avoids the use of ionic species (i.e. mineral acids or fluoride) that compromise the poling process.

## SOL-GEL PROCESSED NLO THIN FILMS



ORGANIC CHROMOPHORE IS AN INTEGRAL COMPONENT OF MATERIAL  
(NO PHASE SEPARATION OR REFRACTIVE INDEX MATCHING NECESSARY)

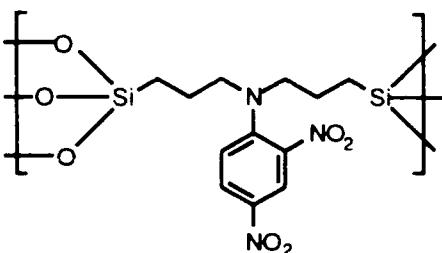
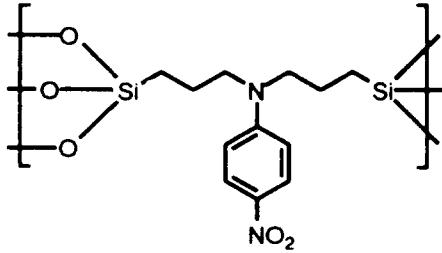
HIGH DENSITY OF CHROMOPHORE

HIGH DEGREE OF CROSSLINKING

Both poling and quantitative evaluation of the NLO response was performed in collaboration with Professor William Steier's group in the Department of Electrical Engineering at USC.

The results of these studies, specifically the  $r_{33}$  and  $d_{33}$  coefficients, are summarized in the following table.

## **$d_{33}$ and $r_{33}$ Coefficients of Poled Sol-Gel Films**

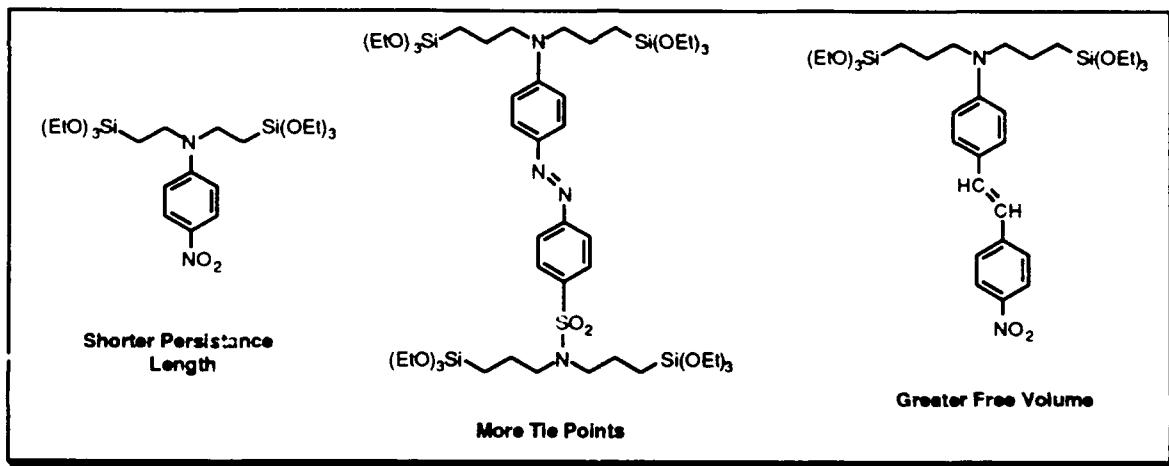
	$d_{33}$ (pm/V)	$r_{33}$ (pm/V)
	9-10	2-2.5
	35-37	9-10
<b>Lithium Niobate <math>\text{LiNbO}_3</math> (bulk)</b>	44	29

We are extremely encouraged that with our first generation monomers, we have produced optical quality films with NLO coefficients comparable to lithium niobate. The  $d_{33}$  coefficient is the highest reported for a p-nitro aniline based material.

We have not however, produced a NLO material that is *optically* stable at temperatures of 150 °C. A plot of the NLO signal response of a poled film of monomer **1** decays significantly upon heating to 150 °C over a period of 60 minutes. The form of the decay curve suggests that a composite of rate constants contribute to the decay. Our analysis of this observation is that the condensed polysilsesquioxane film has sufficient free volume to permit conformational rotation of the optiphore, resulting in loss of the net orientation of the dipoles achieved during poling. Support for this analysis arises from the observation that *the NLO signal can be recovered upon heating to 150 °C and repoling*. The reversibility of the NLO signal establishes that material degradation is not responsible for loss of signal intensity. This latter point is also confirmed by both UV and IR analysis of thin films that have been taken through heating (150 °C) and cooling cycles. These results have been submitted for publication.<sup>3</sup>

We believe that the loss of NLO signal intensity at elevated temperatures as a result of the conformational mobility of the polysilsesquioxane segments can be corrected at the molecular level of design. The approaches we are exploring include monomers with a higher level of functionality (tie points), monomers with a shorter persistence length or a greater chromophore free volume to retard the conformational relaxation of the condensed xerogel. Several second generation monomers shown in the figure below have now been prepared and we are working out the details of a collaboration to evaluate the thin films with Professor Prasad at SUNY Buffalo.

#### SECOND GENERATION NLO MONOMERS



#### Synthesis of Polysilsesquioxanes Doped with Quantum Sized Semiconductor and Transition Metal Particles. Potential NLO Applications.

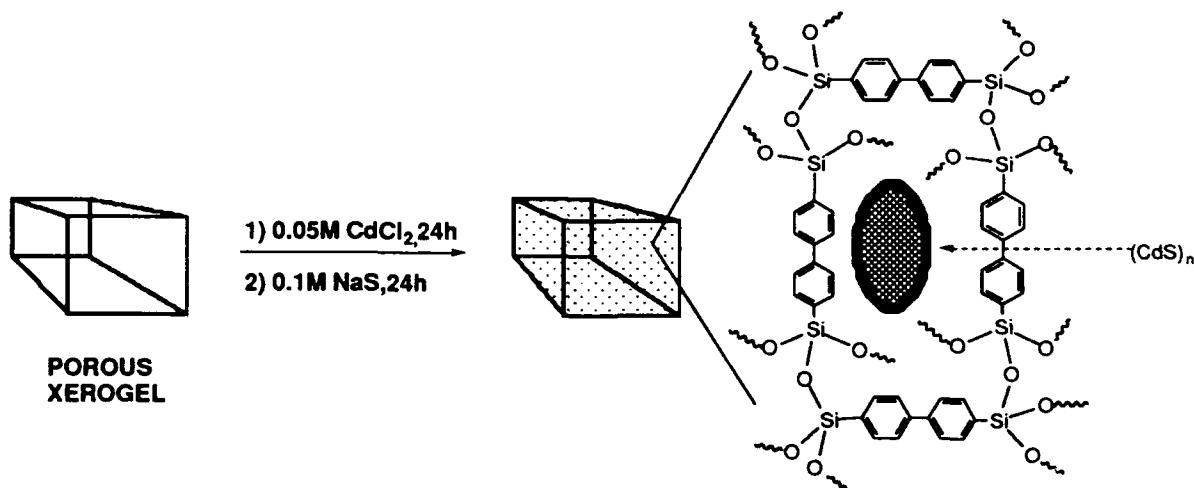
Polysilsesquioxane xerogels provide a family of porous materials with pore sizes that range from the micropore to low mesopore domain (8-100 Å). Depending upon the choice of monomer and processing conditions, a quite narrow distribution of pores can be obtained.

We have explored the opportunity to utilize these porous xerogels as a confinement matrix for the growth of quantum-sized semi-conductor and transition metal particles.

These doped materials may have a number of applications but perhaps most relevant to the Air Force program is their NLO properties. Reports of quantum sized clusters of CdS and transition metals with high  $\chi^3$  behavior have appeared in the recent literature.<sup>6</sup> We have demonstrated that polysilsesquioxanes can serve as a confinement matrix for the growth of

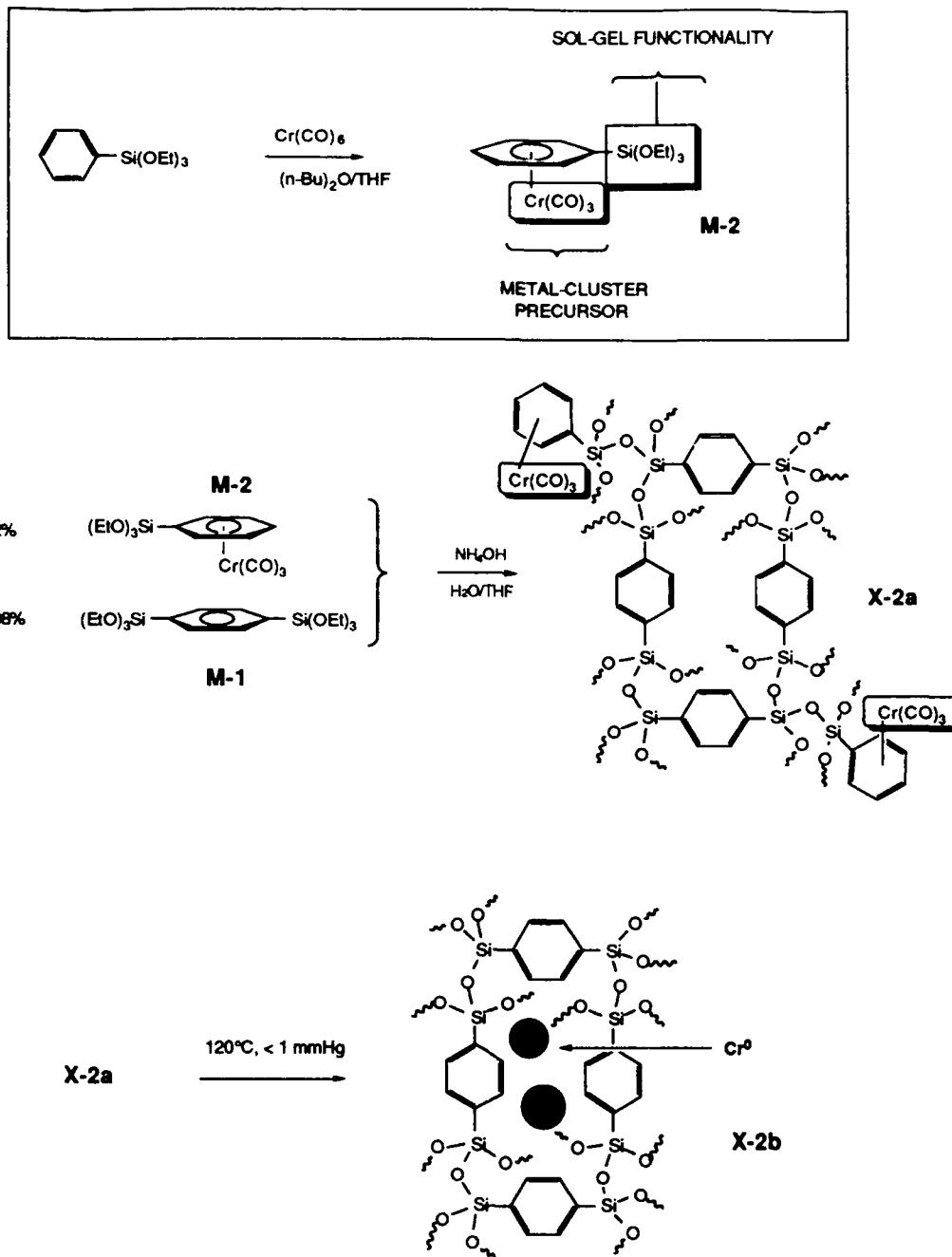
quantum sized semiconductor particles (see figure below).<sup>7</sup> The average size of the semiconductor particles depends in part upon the polysilsesquioxane xerogel used which is ultimately related to the choice of molecular building block.<sup>8</sup> Details of their synthesis and characterization are described in the publications.

**POLYSILSESQUIOXANES AS A CONFINEMENT MATRIX TO CONTROL GROWTH OF Q-SIZED SEMICONDUCTOR AND TRANSITION METAL PARTICLES**



Since the xerogels are optically transparent glasses, evaluation of their nonlinearity is possible and this work is now in progress.

Perhaps even more interesting is the opportunity to incorporate quantum sized transition metal clusters in the xerogels using a novel internal doping technique. The xerogels are made as described previously. However, sol-gel processable transition metal aryl tricarbonyl (M-2) is also incorporated into the matrix. The metal carbonyl is decomposed under relatively mild conditions (150 °C) under high vacuum to deposit quantum sized chromium metal clusters. Our technique is illustrated in the following figure. The details of this will appear in a full paper on this work.<sup>9,10</sup>



The internal doping technique has stimulated our interest in the fabrication of optically transparent thick films that contain "quantum sized" chromium clusters or low dimensional metallic chromium phases. A sample of thick film xerogel doped with chromium is enclosed. A preliminary evaluation of the  $\chi^3$  behavior by 4 wave mixing (a collaboration with Professor Ara Apkarian in the Chemistry Department at UCI) is that the  $\chi^3$  value approaches that of polyacetylene! The origin of the  $\chi^3$  behavior value is the topic of current research.

### *References*

1. (a) Shea, K.J.; Loy, D.A.; Webster, O. *Chemistry of Materials*, **1989**, *1*, 572.  
(b) Shea, K.J.; Webster, O.W.; Loy, D.A. "Better Ceramics Through Chemistry IV", MRS Symposium Proceedings, **1990**, *180*, 975.
2. (a) Shea, K.J., Loy, D.A.; Webster, O. *J. Am. Chem. Soc.*, **1992**, *114*, 6700.  
(b) Loy, D.A.; Shea, K.J.; Russic, E.M. "Better Ceramics through Chemistry V", MRS Symposium Proceedings, **1992**, *271*, 699.
3. Loy, D.A., Shea, K.J.; Small, J.H. *Journal of Non-Crystalline Solids*, **1993**, *160*, 234.
4. Oviatt, H.W., Jr.; Shea, K.J.; Small, J.H. *Chemistry of Materials*, **1993**, *5*, 943.
5. Oviatt, H.W., Jr.; Shea, K.J.; Kalluri, S.; Shi, Y.; Steier, W.N.; Dalton, L.R. *Chemistry of Materials*, submitted for publication.
6. (a) Fukumi, K.; Chayahara, A.; Kohei, K.; Sakaguchi, T. *J. Appl. Phys.*, **1994**, *75*, 3075.  
(b) Li, C.-Y.; Wilson, M.; Haegel, N.; Mackenzie, J.D.; Knobbe, E.T. MRS Symposium Proceedings, **1992**, *272*, 41.  
(c) Spanhel, L.; Schmidt, H.; Uhrig, A.; Klingshirn, C. MRS Symposium Proceedings, **1992**, *272*, 53.
7. Choi, K.M.; Shea, K.J. *Chemistry of Materials*, **1993**, *5*, 1607.
8. Choi, K.M.; Shea, K.J. *J. Phys. Chem.*, **1994**, *98*, 3207.
9. Choi, K.M.; Shea, K.J. "Better Ceramics through Chemistry VI", MRS Symposium Proceedings, **1994**, in press.
10. Choi, K.M.; Shea, K.J. *J. Am. Chem. Soc.*, **1994**, *116*, 0000.

## **Students Who Have Worked or Are Working on the Project**

**Henry Oviatt - Graduate Student (Ph.D. 1994)**

**James Small - Graduate Student**

**Stephen Hobson - Graduate Student**

**Joseph Tran - Graduate Student**

**Kyung M. Choi - Postdoctoral**

**Sean McHugh - Undergraduate Student**

In addition to the students mentioned above, this research program has resulted in collaborations with the following research groups:

**Dr. Doug Loy - Sandia National Laboratory**

**Professor Larry Dalton - Department of Chemistry, USC**

**Professor William Steier - Department of Electrical Engineering, USC**

**Professor Ara Apkarian - Department of Chemistry, UCI**

**Professor P. Prasad - Department of Chemistry, SUNY Buffalo**

## **Papers and Invited Lectures**

Since July 1992 my group and collaborators have presented 16 papers at national and international symposia, and I have been an invited speaker at 11 national and international symposia, government and industrial research laboratories, and academic institutions on work supported by the Air Force Office of Scientific Research grant F49620-92-J-0379.

**Publications Resulting from Air Force Support  
(F49620-92-J-0379)**

1. Loy, D.A., Shea, K.J.; Small, J.H. "Arylene- and Alkylene-Bridged Polysilsesquioxanes," *Journal of Non-Crystalline Solids*, **1993**, *160*, 234.
2. Oviatt, H.W., Jr.; Shea, K.J.; Small, J.H. "Alkylene-Bridged Silsesquioxane Sol-Gel Synthesis and Xerogel Characterization. Molecular Requirements for Porosity," *Chemistry of Materials*, **1993**, *5*, 943.
3. Choi, K.M.; Shea, K.J. "New Materials for Synthesis of Quantum-Sized Semiconductors and Transition-Metal Particles. Microporous Polysilsesquioxanes as a Confinement Matrix for Particle Growth," *Chemistry of Materials*, **1993**, *5*, 1607.
4. Choi, K.M.; Shea, K.J. "Amorphous Polysilsesquioxanes as a Confinement Matrix for Quantum-Sized Particle Growth. Size Analysis and Quantum Size Effect of CdS Particles Grown in Porous Polysilsesquioxanes," *J. Phys. Chem.*, **1994**, *98*, 3207.
5. Choi, K.M.; Shea, K.J. "Preparation and Characterization of Ultra-Small Sized Metal and Semiconductor Particles in Sol-Gel Materials," "Better Ceramics through Chemistry VI", *MRS Symposium Proceedings*, **1994**, in press.
6. Choi, K.M.; Shea, K.J. "Preparation of Nano-Sized Chromium Clusters and Intimate Mixtures of Chromium/CdS Phases in a Porous Hybrid Xerogel by an Internal Doping Method," *J. Am. Chem. Soc.*, **1994**, *116*, 0000.
7. Oviatt, H.W., Jr; Shea, K.J.; Kalluri, S.; Shi, Y.; Steier, W.N.; Dalton, L.R. "Applications of Organic Bridged Polysilsesquioxane Xerogels to Nonlinear Optical Materials by the Sol-Gel Method," *Chemistry of Materials*, submitted for publication.